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SILVER-BASED COMPOSITE INORGANIC ANTIMICROBIAL AGENT
[Zi Yin Shee Leeuh Foo Huh Woo Jee Kahng Joon Jee Jee chee Jiree Bay]

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Claims

1. A silver-based composite inorganic antimicrobial agent, characterized in that composite phosphate is used as a carrier of inorganic silver-based antimicrobial agent, and the particle size thereof is uniform and less than 0.5μm.

2. The silver-based composite inorganic antimicrobial agent according to Claim 1, characterized in that the pH value is 6-8.

3. The silver-based composite inorganic antimicrobial agent according to Claim 1, characterized in that the carrier is $M_1M_2(PO_4)_3 \cdot nH_2O$ composite phosphate, in which M_1 is one or two of mono-valent ions comprising Na^+, K^+, Rb^+, Cs^+, NH_4^+ and H^+, and M_2 is one or two of tetravalent metal ions comprising titanium, zirconium and tin, the synthesis time of the carrier is 2-10 h; and the reaction temperature is controlled within 100°C.

4. The silver-based composite inorganic antimicrobial agent according to Claim 1, characterized in that a main antimicrobial ingredient is bivalent or trivalent silver salt.

5. The silver-based composite inorganic antimicrobial agent according to Claim 1, characterized in that the preparation process thereof consists of the following steps: preparing composite phosphate carrier, preparing silver salt, and preparing and post-treating silver high-valent oxidative compound.

5. [sic; 6] A preparation of the silver-based composite inorganic antimicrobial agent according to Claim 4, characterized in that the composite phosphate carrier introduces a silver antimicrobial component by ion-exchange method, adsorption method, and reduction and oxidation method.

6. [sic; 7] The preparation of the silver-based composite inorganic antimicrobial agent according to Claim 4, characterized in that the time for heat treatment is 2-10 h, the calcination temperature is below 1100°C.

8. The preparation of the silver-based composite inorganic antimicrobial agent according to Claim 4, characterized in that air vibrating screen is used for stage treatment so as to make the product particle size less than 0.5μm.

The present invention relates to a silver-based composite inorganic antimicrobial agent and preparation thereof.

It is well known that silver ion, copper ion, zinc ion, etc. have antimicrobial properties. For example, silver ion is present in the form of silver nitrate solution, and extensively used as disinfectant and antimicrobial agent, but it is not convenient to use in liquid state, which limits its application. Therefore, there is an urgent market demand for a solid antimicrobial agent containing metal ions. At present, there are many reports on relevant antimicrobial materials and their preparations such as preparation of antimicrobial zeolite with small tarnishing capacity and preparation of antimicrobial zeolite. But these kinds of antimicrobial zeolite are not very stable if they carry silver ion as antimicrobial metal ion; accordingly, it is proposed that the addition of various stabilizers into the product can improve its stability and weathering resistance. For example, a composition of antimicrobial zeolite and resin carrying silver ion can be added with benzotriazole compound, acid acetylamino compound or others, but these compositions and substances made from the compositions become unstable at 300°C, with larger tarnishing probability, and are weakly toxic, especially in paint. So far, there have been many

proposals about stabilizers for preventing the tarnishing of antimicrobial agent and its composition. However, these stabilizers cannot fully inhibit the tarnishing, the average particle size of the stabilizers is more than several microns, and the granularity is widely distributed; therefore, their dispersibility, especially in resin, is very poor; if used in fiber as thin as several microns, breakage will often occur during spinning.

The invention aims to provide a silver-based composite inorganic antimicrobial agent with very uniform and fine particles, and its preparation.

To achieve the aim described above, a silver-based inorganic antimicrobial agent of the invention employs composite phosphate as a carrier of inorganic silver-based antimicrobial agent, and its size is uniform and less than 0.5μm.

A silver-based composite inorganic antimicrobial agent of the invention has a pH value of around 8, and its carrier employs $M_1M_2(PO_4)_3 \cdot nH_2O$ composite phosphate, in which M_1 is one or two of mono-valent ions such as Na^+, K^+, Rb^+, Cs^+, NH_4^+ and H^+; M_2 is one or two of tetravalent metal ions such as titanium, zirconium and tin; the synthesis time of the carrier is 2-10 h; the reaction temperature is controlled within 100°C; and the main antimicrobial ingredient is bivalent or trivalent silver salt.

The preparation process of the silver-based composite inorganic antimicrobial agent of the invention is composed of following steps: preparation of composite phosphate carrier, preparation of silver salt, preparation of silver high-valent oxidative compound and post-treatment.

The preparation of the invention: the composite phosphate carrier uses ion-exchange method, adsorption method, and reduction and oxidation method to introduce an antimicrobial component such as silver. The post-treatment is mainly heat treatment and stage treatment. The heat treatment time is

2-10 h, and the calcination temperature is below 1100°C. An air vibrating screen is used for stage treatment to make the product particle size less than 0.5μm.

The invention uses high-valent silver ion to replace prior mono-valent silver ion as an antimicrobial ingredient, because the bi-valent silver and tri-valent silver antimicrobial agents have 50-200 times the capability of mono-valent silver or metal silver, and they act more quickly. Thus on the one hand, the invention solves the problems of high cost and great consumption of inorganic antimicrobial agent; on the other hand, the extremely high reduction potential of silver in high oxidative state can improve the epiphyte sterilization by producing active oxygen atoms in its surrounding space. During the heat treatment, the use of high temperature calcination can improve its weathering resistance and not lower its antimicrobial effect. A super thinning treatment to the composite phosphate carrier can make its size uniform and surface areas increase, accordingly, effectively improving the antimicrobial effect of the antimicrobial agent.

Embodiment 1

1. Preparation of the composite phosphate carrier

Preparation of potassium-type composite phosphate: add 0.1 mol sodium citrate solution into 0.2 mol titanyl sulfate aqueous solution while stirring, then add 0.3 mol H_3PO_4 or NaH_2PO_4 solution, adjust its pH value with KOH aqueous solution to about 5, and reflux at 95°C for 10 h, with continuous stirring. Filter precipitate, wash with water, and dry to give netlike composite salt of potassium titanium phosphate, with an average particle size of less than 0.5μm.

2. Preparation of salt silver

Add potassium-type titanium phosphate salt powder obtained in 1 into aqueous solution with a proper amount of $AgNO_3$ dissolved therein, stirring at 60°C for 10 h to obtain a slurry. Wash the slurry with pure water after filtration, then dry it at 110°C overnight.

3. Preparation of low-valent silver oxide

Calcine semi-finished material prepared in 2 at 800-1100°C for 2-10 h, crushed down, to obtain an antimicrobial agent of low-valent silver.

4. Preparation of high-valent silver oxidative compound

(1) Disperse well 0.3 mol product prepared in 2 or 3 into water, and add a mixture of 0.02 mol potassium persulphate or sodium persulphate and 0.08 mol potassium hydroxide or sodium hydroxide while stirring. The reactants described above are reacted at 20-80°C for 4-10 h, filtered, washed and dried to obtain an antimicrobial agent containing tri-valent silver. Alternatively, the reactants described above are reacted with phosphate or hydrofluoric acid to obtain an antimicrobial agent containing bi-valent silver.

(2) The antimicrobial agent containing high-valent silver goes through heat treatment at 400-1100°C for 2-8 h, to improve weathering resistance while not reducing its antimicrobial effect.

5. Post-treatment

This process is to carry out air vibrating screen for the prepared antimicrobial agent, ensuring its size is uniform and less than 0.5μm. Because some water is brought in during the process of air vibrating screen, the powder further requires a low-temperature drying treatment at about 100°C.

Some major technical indicators of the antimicrobial agent of the invention:

Main ingredients: ion-exchanger substituted with silver

Appearance: white powder

Particle size (μm): < 0.5

Specific gravity (g/cm^3): 3.0

pH value: 6-8

Loss by drying (%): < 0.08

Loss by calcination (%): < 0.1